

PHASE TRANSITIONS IN POLYMERIC AND MICELLAR SYSTEMS

Summer School on Neutron Scattering and Reflectometry

NG3 SANS Team

NIST Center for Neutron Research

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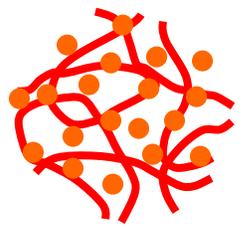
ABSTRACT

Small-Angle Neutron Scattering (SANS) will be used to characterize the solution structure and phase transitions of a water-soluble triblock copolymer. At low temperature, the copolymer behaves as a polymer solution, but at higher temperature it undergoes a transition that forms micelles. These micelles have found application in pharmaceuticals. You will learn all aspects of collecting a complete set of SANS measurements, including sample preparation, instrument setup, and the required measurements. After collecting your raw SANS data, you will learn how to correct and reduce the data into a form that can be analyzed. Data analysis will include simple standard plot methods and realistic models used to fit the reduced data. Guinier analysis, form factor scattering, and inter-particle interactions will be described. The phase behavior and microstructure formation common to surfactant and polymer systems will be compared.

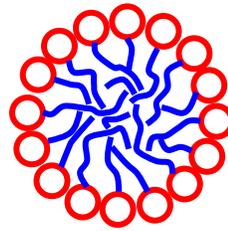
1. INTRODUCTION

The most active Small-Angle Neutron Scattering (SANS) research areas are in “Polymers” and “Complex Fluids” which include micellar systems. Understanding the thermodynamics of mixing of polymers and/or complex fluids is important. This involves insight into the major phase transitions and the various structures that are formed.

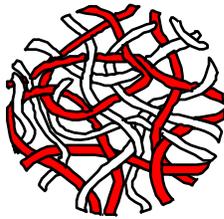
Polymer mixtures consist of polymer solutions, polymer blends, copolymers as well as their mixtures. Micelles are formed when a surfactant, oil and water are mixed. Adding oil forms a microemulsion. These systems form structures in the nanometer length scale that can be quantified by the SANS technique.



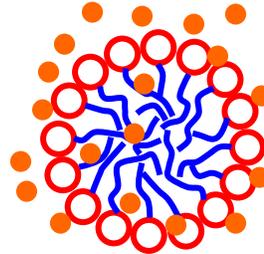
Polymer Solution



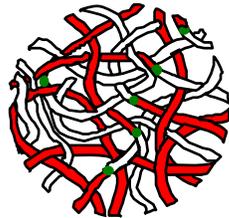
Binary Micelle



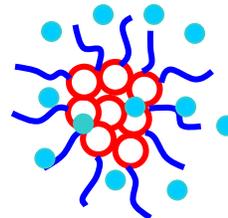
Polymer Blend



Ternary Micelle



Block Copolymer



Reverse Micelle

Figure 1: Various polymeric and micellar systems. The small dots represent solvent molecules.

2. PHASE TRANSITION BASICS

Polymer mixtures phase separate either through cooling and are characterized by an Upper Critical Spinodal Temperature (UCST), or upon heating and are characterized by a Lower Critical Spinodal Temperature (LCST). Combinations of LCST and UCST are also possible.

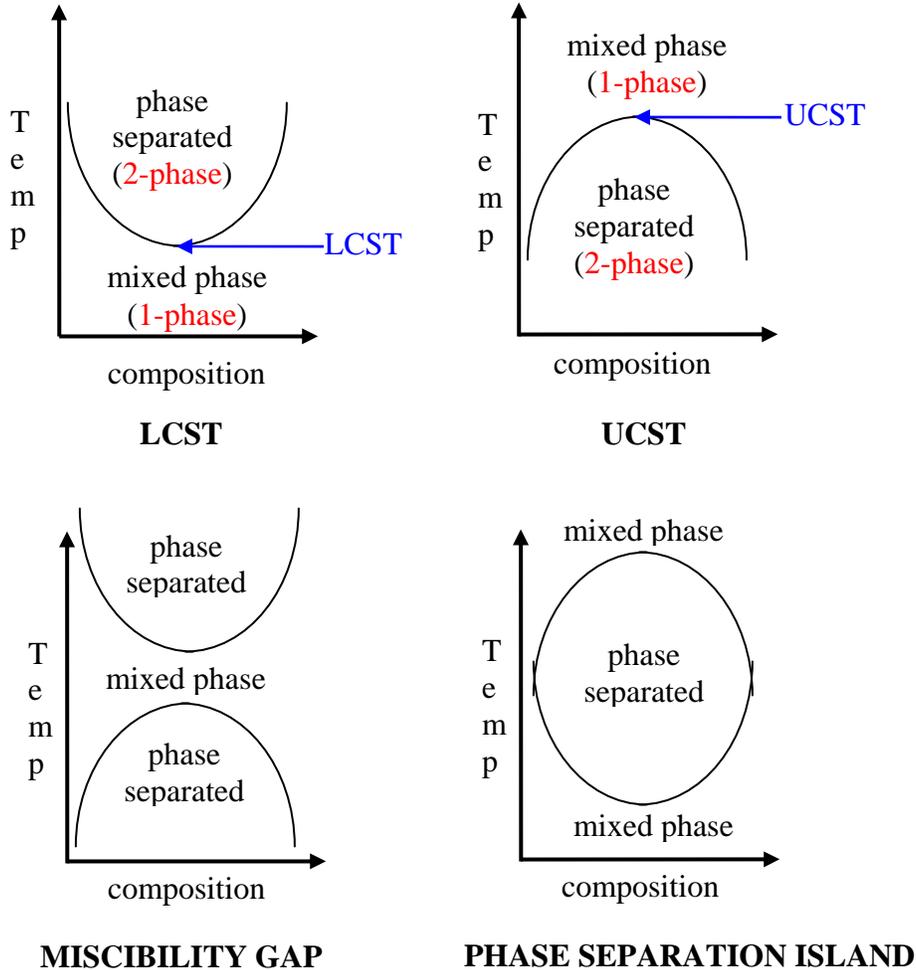


Figure 2: Various possible phase diagrams.

Composition fluctuations are enhanced when phase transition lines are approached from the mixed (1-phase) region. This increases the SANS intensity thereby making this technique an appropriate probe for thermodynamic (phase transition) studies.

The “binodal” condition is the phase transition line between the homogeneously mixed 1-phase region and the phase separated (i.e., demixed) 2-phase region in the temperature-composition phase diagram. The spinodal line is the deeper part of the demixed 2-phase region. The region between the binodal and the spinodal lines is the nucleation-and-growth region while the region within the spinodal line is the spinodal region. Most water-soluble systems phase separate upon heating due to the softening of hydrogen-bonding at elevated temperatures.

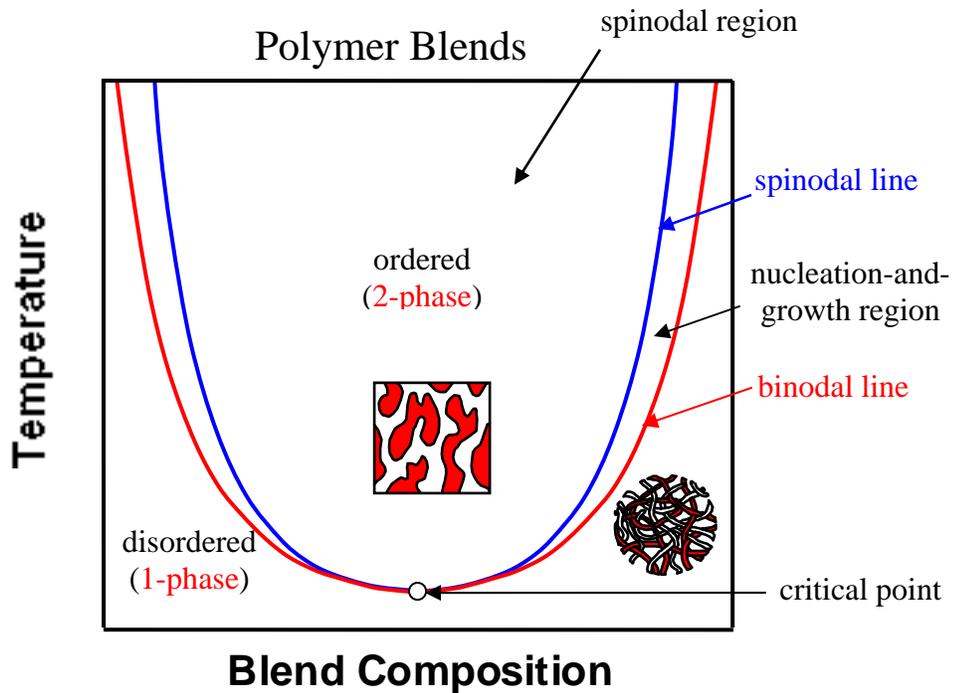


Figure 3: Schematic representation of the phase diagram for polymer blends.

For block copolymers, the spinodal line is referred to as the Order-Disorder-Temperature (ODT). The ODT defines a region which comprises three main forms of microphase separation; these correspond to spherical, cylindrical and lamellar morphologies. The LCST line is referred to as the Lower Critical Ordering Temperature (LCOT) for copolymers. The copolymer composition is varied by increasing the length of one of blocks in the copolymer.

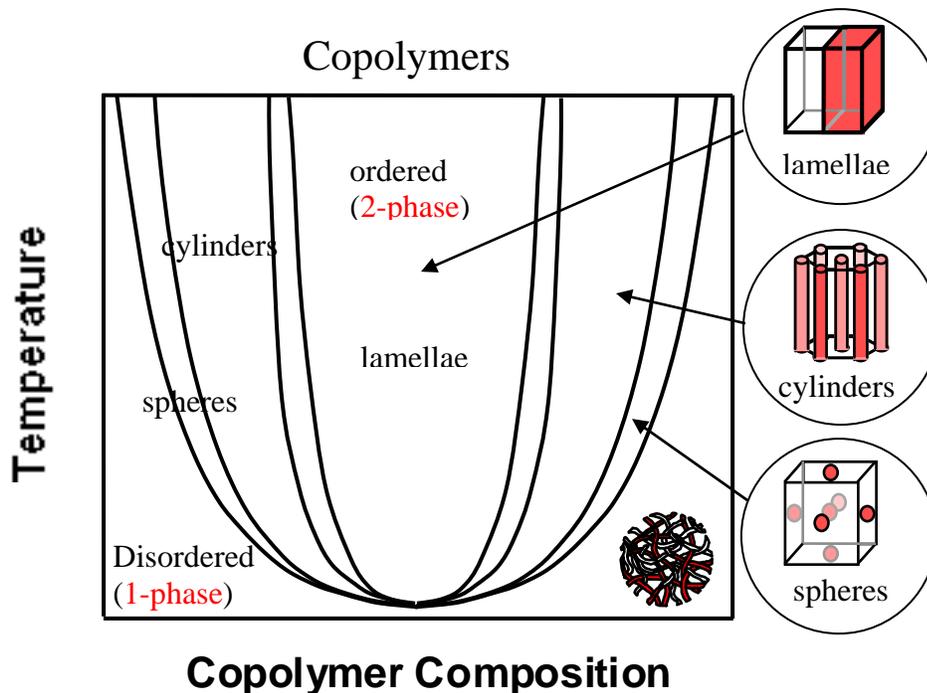


Figure 4: Representation of the various copolymer microphases for a Lower Critical Ordering Temperature (LCOT) system.

Surfactants are amphiphilic molecules which contain a hydrophilic part and a hydrophobic part. Surfactants can be ionic when the hydrophilic part of the molecule is charged. They can also be nonionic when the molecule is completely uncharged. When surfactants are mixed with water and are above a certain concentration and temperature, they form micelles in solution. The concentration threshold is called the Critical Micelle Concentration (CMC) and the temperature threshold is the Critical Micelle Temperature (CMT). One example of a nonionic surfactant is a Pluronic copolymer described next.

3. WHAT ARE PLURONICS?

Poly(ethylene oxide) (referred to as PEO) is the simplest water soluble polymer and has the structure $-\text{CH}_2\text{CH}_2\text{O}-$. Its neighbor in the homologous series poly(propylene oxide) (or PPO) does not dissolve in water at ambient temperature. Pluronics are triblock copolymers composed of one central PPO block connected to two PEO blocks. The PEO block dissolves well in aqueous media because it is mostly hydrophilic, while the PPO block does not dissolve because it is mostly hydrophobic at ambient temperature. This amphiphilic nature of pluronic molecules makes them form micelles at ambient temperature. At low temperatures, this balance does not hold and both PEO and PPO blocks dissolve in water thereby remaining individual molecules. Pluronics are commercially available materials used in the cosmetics and pharmaceutical industries. The CMT and CMC vary depending on the block composition of the various pluronics which allows selection of the optimal surfactant for the desired application. The P85 pluronic considered here consists of 26 EO monomers in each of the outside blocks and 40 PO monomers in the middle block. P85 is referred to as $\text{EO}_{26}\text{PO}_{40}\text{EO}_{26}$. The molecular weight of P85 is around 4,600 g/mol.

4. SANS FROM P85 PLURONIC

The interest here is in micelle-formation as well as in the investigation of phase transitions that form various microstructures. A series of P85 samples of different weight fractions in D_2O (d-water) were prepared and measured by SANS.

In order to investigate micelle formation, SANS data were taken from 10 % by weight P85 in deuterated water (d-water) at various temperatures (from 10 °C to 60 °C). D-water was used in order to enhance the neutron contrast. Micelles are well formed at 30 °C. When micelles are formed, the scattering is characterized by two features: a peak characteristic of inter-micelles interactions, and decay at high Q characterizing the tail of the single-particle form factor. In-between these two features, a second shoulder (around $Q = 0.15 \text{ \AA}^{-1}$) can be observed. This shoulder is also characteristic of the single particle form factor (oscillation of the spherical Bessel function) and is more or less visible depending on the size polydispersity of the micelles.

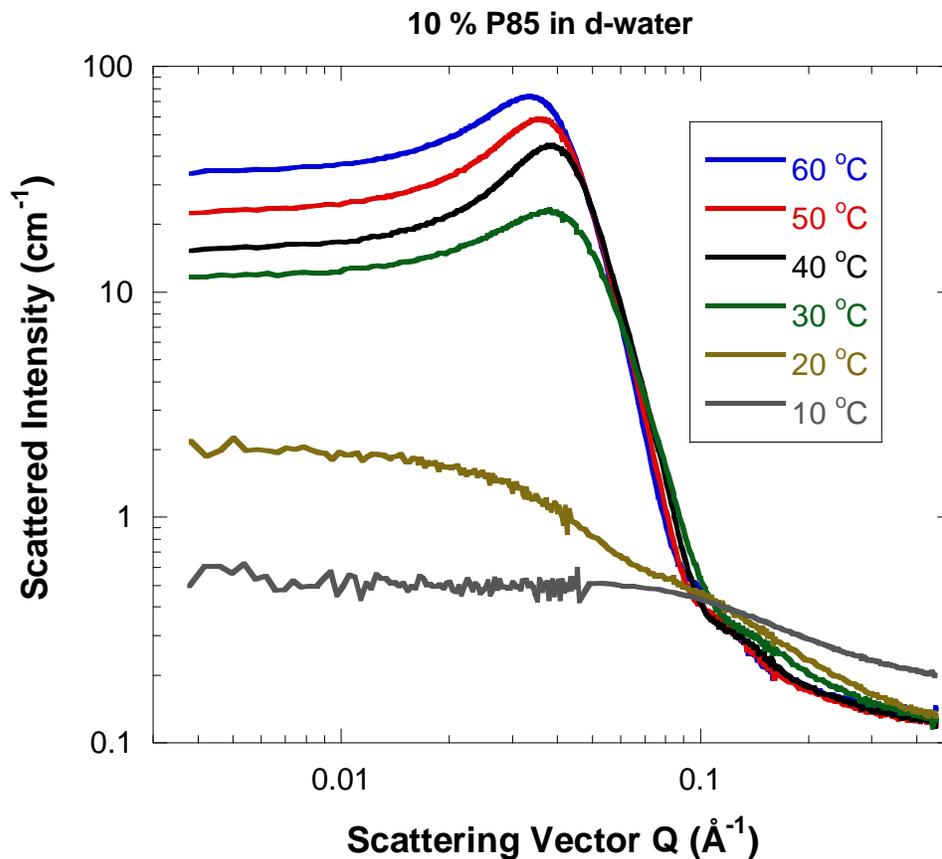


Figure 5: SANS data from the 10 % by weight P85 in D_2O at various temperatures. Data statistics are different for the two instrument configurations. The overlap region for the two SANS configurations used is around 0.04 \AA^{-1} .

In order to determine the Critical Micelle Temperature, the SANS intensity at a low Q value ($Q = 0.02 \text{ \AA}^{-1}$ is chosen) is plotted with increasing temperature. The CMT is seen to be around $22 \text{ }^\circ\text{C}$ for the 10 % by weight P85/d-water sample. This characteristic temperature is observed as a jump in the low- Q intensity.

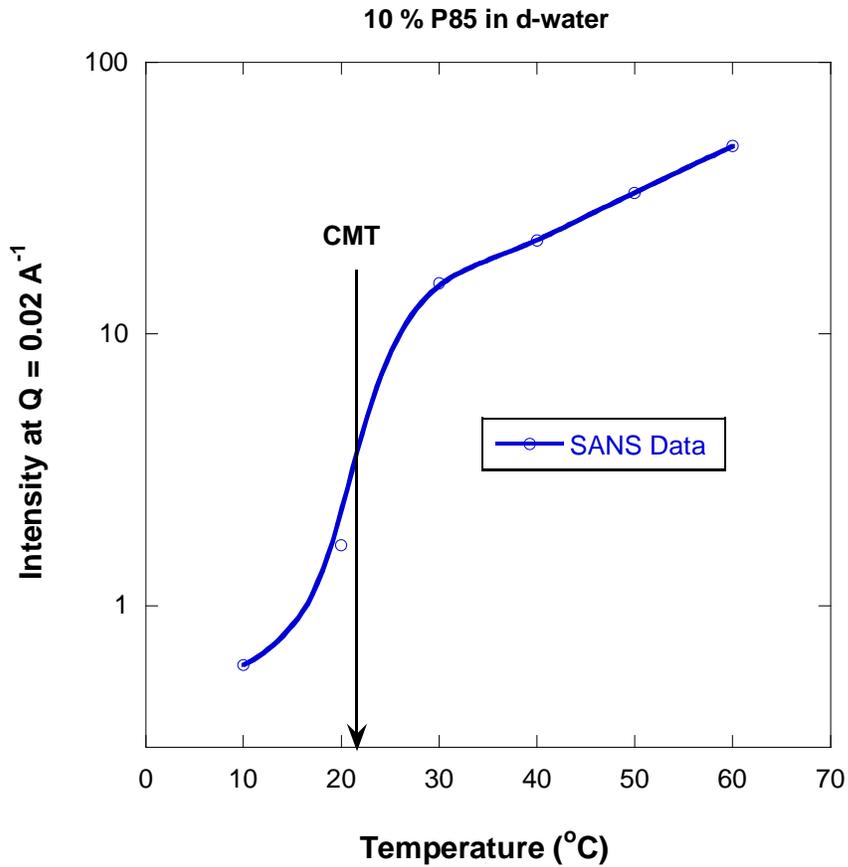


Figure 6: Sigmoid shape variation of the low-Q SANS intensity with temperature for the 10 % by weight P85/d-water sample.

SANS data are shown also for a 1 % by weight P85/d-water sample for a wider temperature range (10 °C to 80 °C). The low P85 weight fraction allows the observation of the single-particle form factor without interference from the inter-particle interaction peak. The intensity is seen to increase with increasing temperature but the shape of the form factor changes from unimers (below the CMT), to spherical micelles then to cylindrical micelles.

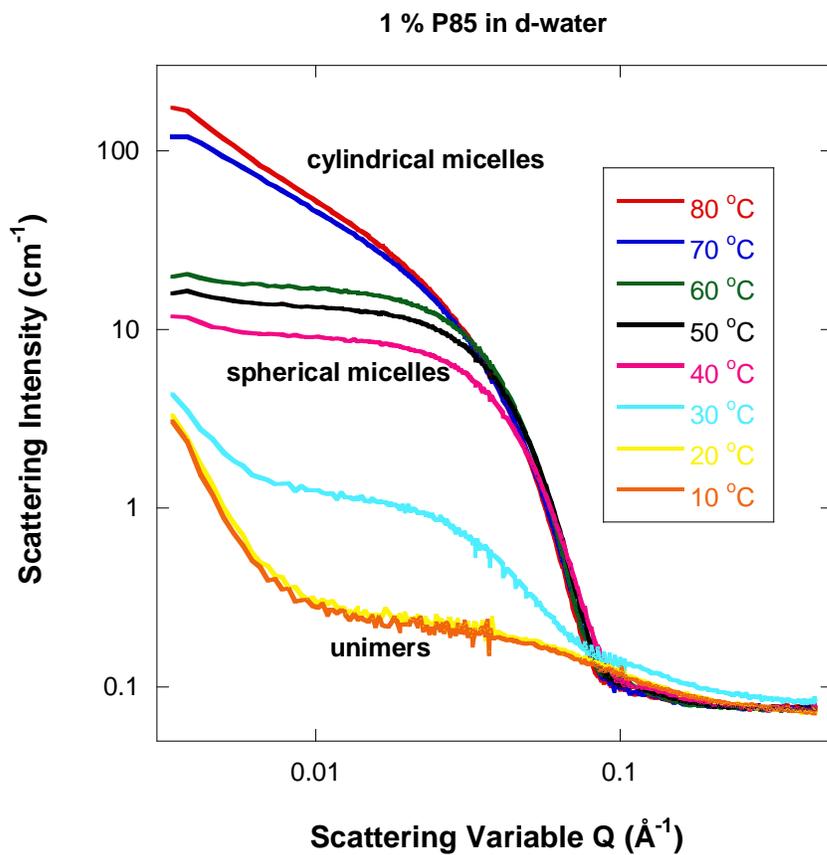


Figure 7: SANS intensity increase pointing to the three observed structures (unimers, spherical micelles and cylindrical micelles).

Here also, a plot of the low- Q SANS intensity shows clearly the transition temperatures between the observed phases. Heating and cooling cycles show that these phase transitions are reversible.

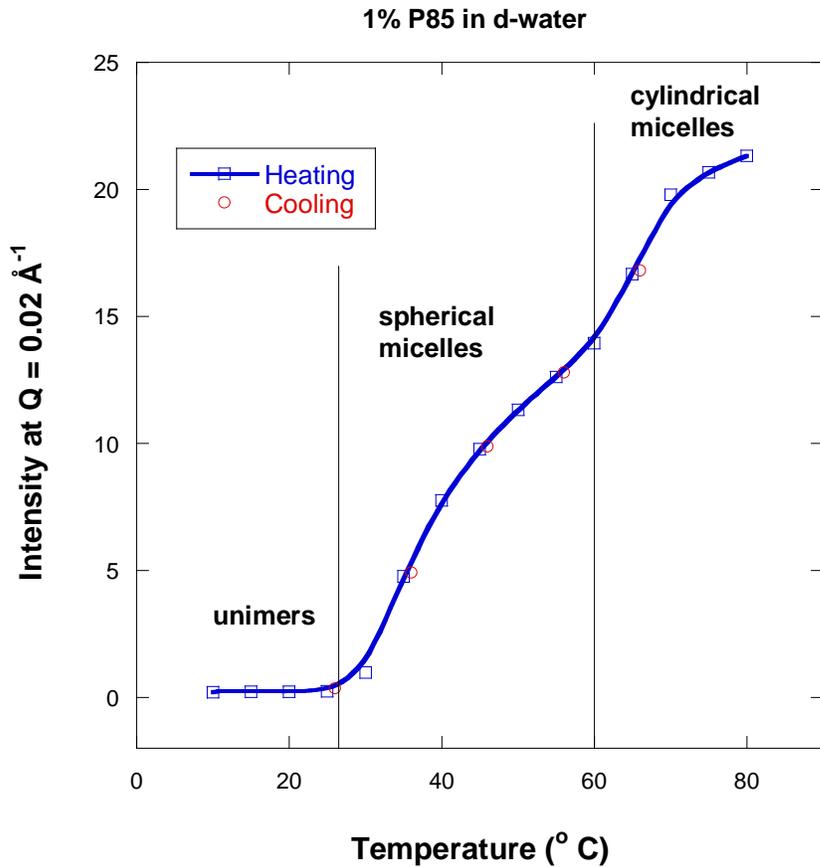


Figure 8: Variation of the low-Q SANS intensity for increasing temperature for the 1 % by weight P85/d-water sample.

5. THE P85/D-WATER PHASE DIAGRAM

The P85/d-water phase diagram has been mapped out (Mortensen, 1996) using the SANS technique (among other techniques). The main phases (unimers, spherical micelles and cylindrical micelles) can be observed at low P85 weight fraction. Other phases (lamellar micelles, ordered spherical micelles, and a disordered phase) are not discussed here.

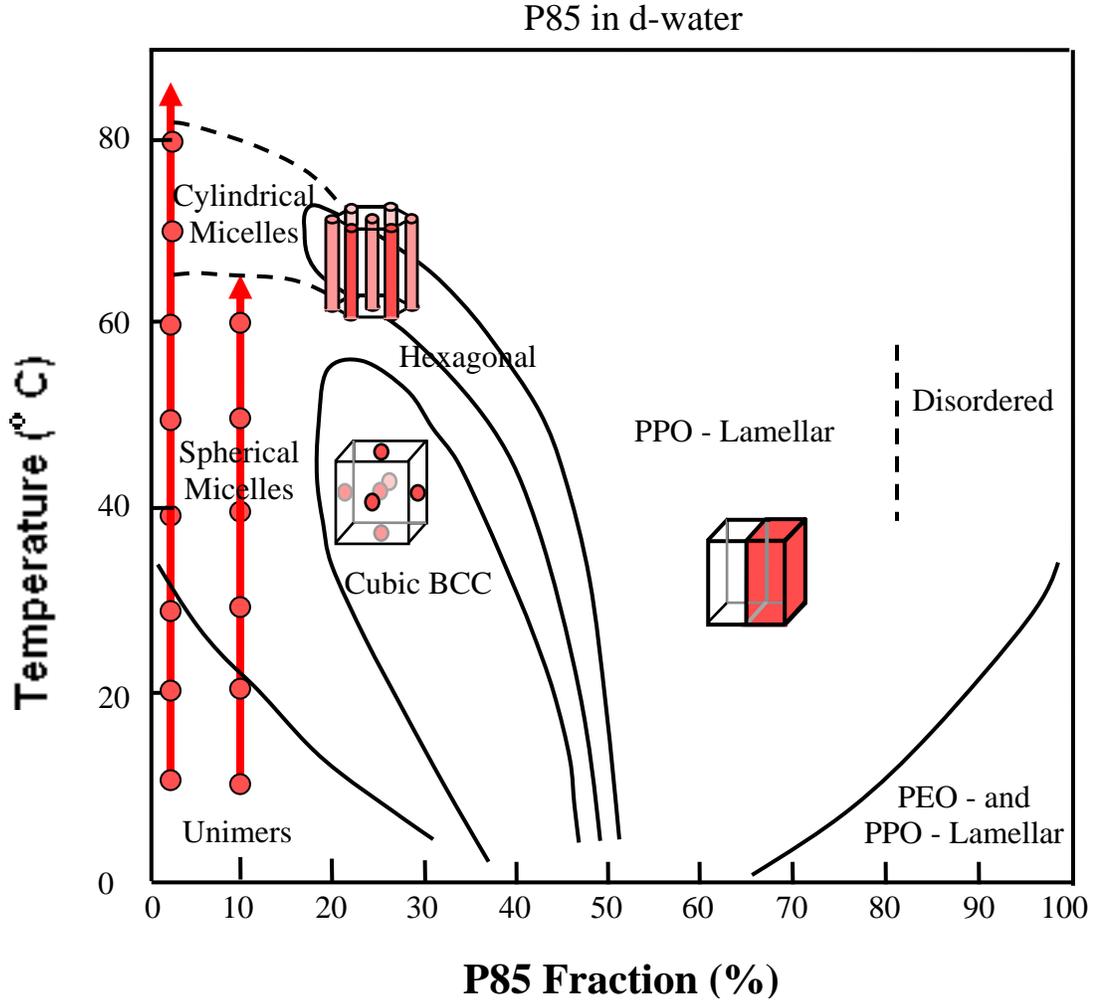


Figure 9: The P85/d-water phase diagram.

6. MICELLAR STRUCTURES MODEL

At low P85 weight fraction, spherical micelles and then cylindrical micelles form with increasing temperature. These structures are described here. If we assume that the scattering length density of the micelle is uniform, then the SANS cross section (scattering intensity) can be simplified as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{N}{V}\right) \Delta\rho^2 V_P P(Q) S_I(Q). \quad (1)$$

Here N/V is the micelle number density, $\Delta\rho^2$ is the contrast factor, V_P is the micellar volume, $P(Q)$ is the single micelle form factor and $S_I(Q)$ is the inter-micelles structure factor.

The form factors for a sphere of radius R is:

$$P(Q) = \left[\frac{3j_1(QR)}{QR} \right]^2 = \left[\frac{3}{QR} \left(\frac{\sin(QR)}{(QR)^2} - \frac{\cos(QR)}{QR} \right) \right]^2 \quad (2)$$

And for a randomly oriented cylinder of radius R and length L is given by:

$$P(Q) = \frac{1}{2} \int_{-1}^1 d\mu \left[\frac{\sin(Q\mu L/2)}{Q\mu L/2} \right]^2 \left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R} \right]^2.$$

Here $j_1(x)$ is the spherical Bessel function and $J_1(x)$ is the cylindrical Bessel function of first order.

7. THE TERNARY PHASE DIAGRAM

The phase diagram of a ternary micellar system (Kahlweit and Strey, 1985) is represented by a triangle (A: water, B: oil and C: surfactant). The three binary systems A/B, A/C and B/C are represented by their characteristic mixed phase (1-phase) and phase separated (2-phase) regions. The oil-surfactant (B/C) binary mixture is characterized by an upper critical solution temperature (UCST); i.e., it phase separates upon cooling. The water-oil (A/B) binary mixture is also characterized by a UCST behavior but is mostly phase separated (water and oil do not mix). The phase diagram for the water-surfactant (A/C) binary solution is more complex; it is characterized by a UCST behavior at low temperatures and possibly a closed loop immiscibility island at high temperatures; i.e., it phase separates both upon cooling and upon heating and is usually only observed for nonionic surfactants.

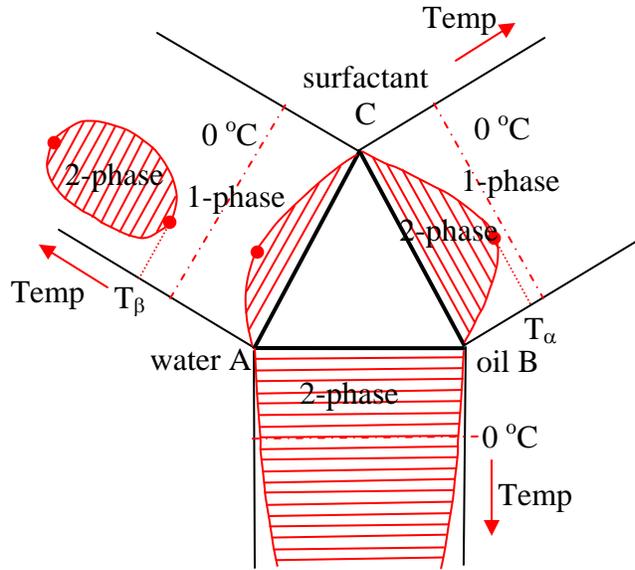


Figure 10: Phase diagram for the three binary mixtures (B/C, A/B, and A/C). The phase separation lines and temperatures are shown. The 0 °C water-freezing line has also been marked.

Phase separation occurs upon jumping from the mixed phase (1-phase) region to the phase separated (2-phase) region. Phase separation proceeds along tie lines and produces a phase rich in the A component (left side) and a phase rich in the C component (right side). The points at which the phase separation lines have a horizontal slope are the critical points. The A/C binary phase diagram shows three critical points. Note that the lower UCST may lie below the freezing point of the mixture.

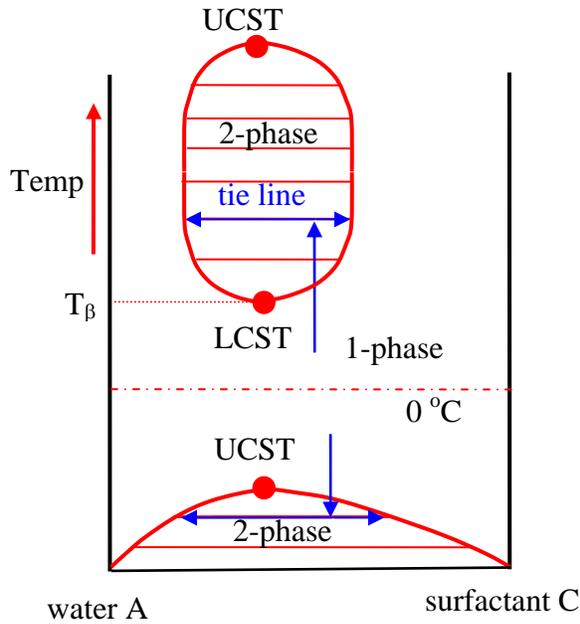


Figure 11: The water/surfactant (A/C) binary phase diagram.

Given the three generic binary mixtures phase diagrams, the phase diagram for the ternary A/B/C mixture is discussed next.

The ABC triangle is obtained by combining the three binary mixtures phase diagrams. It contains a micelle-formation phase (m-phase) region and a 2-phase region. The m-phase region contains structures in the nanometer size scale (oil-in-water and water-in-oil micelles). The 2-phase region contains a phase rich in surfactant/water in equilibrium with an oil-rich phase at low temperatures. At higher temperatures, the surfactant is more soluble in oil and the 2-phase equilibrium is contains a phase rich in surfactant/oil in equilibrium with a water-rich phase. Note that micelles can form in the 2-phase region as well since binary mixtures (water/surfactant or oil/surfactant) can form micelles. The m-phase region is inhomogeneous (contains micelles) in the nanometer size scale but homogeneous in the micrometer (optical range) size scale. The m-phase region is “clear” for light but “cloudy” for neutrons.

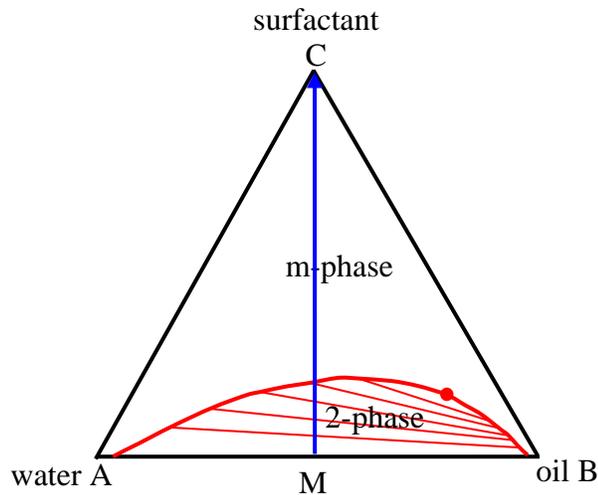


Figure 12: Schematic phase diagram of a generic ternary mixture. The m-phase is the micelle-formation phase.

Note that the case of P85 in d-water described previously corresponds to the left side (AC) of the ternary phase triangle.

This simple representation of the ternary phase diagram is valid for low temperatures; i.e., before reaching the closed loop region in the A/C phase diagram. When the closed loop region is reached, there is an interplay of interactions which adds two 2-phase regions (one water-rich and one oil-rich).

The “fish” phase diagram is obtained when an MC cut is taken across the ABC triangle phase diagram. This cut corresponds to increasing the surfactant concentration but keeping the ratio of water to oil constant. Representation of the temperature/ surfactant fraction phase diagram comprises the m-phase region at high surfactant fraction, two 2-phase regions (at low and high temperatures) and a 3-phase region at intermediate temperatures. The name “fish” stems from the shape of the phase diagram with the 3-phase as the fish head.

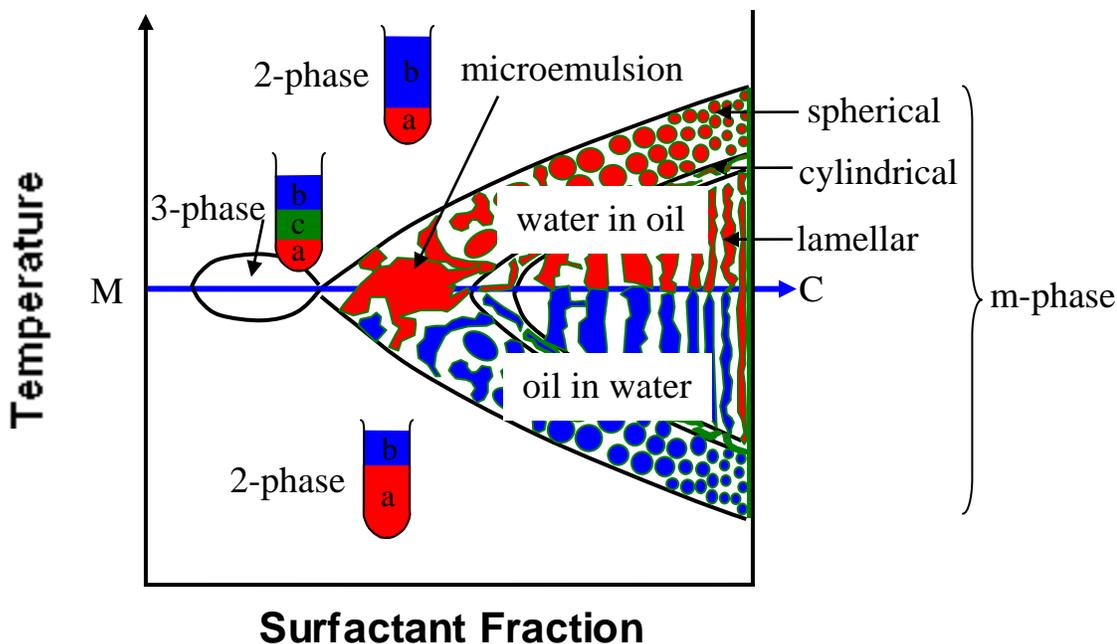


Figure 13: The “fish” phase diagram.

The m-phase region is the focus of most SANS investigations since it is the region of micelle formation. The m-phase region is rich in mesophases (with various morphologies). It contains spherical, cylindrical (also called wormlike) and lamellar micelles depending on the temperature range. Structures for these mesophases correspond to cubic, hexagonal and lamellar symmetry respectively. Note also the “microemulsion” (also called bicontinuous) phase. Moreover, oil-in-water micelles are obtained at low temperature and “reverse” (water-in-oil) micelles are obtained at high temperatures.

This description was based on studies with common oils and water, using “typical” surfactants of low molecular weight. It is interesting to note that much higher molecular weight copolymers can also play the role of surfactants. When A-C block copolymers are mixed with A and B homopolymers (taking the place of “oil” and “water”), the same “fish” phase behavior is obtained.

REFERENCES

M. Kahlweit and R. Strey, “Phase Behavior of Ternary Systems of the Type H₂O-Oil-Nonionic Amphiphile (Microemulsions)”, *Angewandte Chemie International Edition in English* 24, 654–668 (1985).

K. Mortensen, “Structural Studies of Aqueous Solutions of PEO-PPO-PEO Triblock Copolymers: Their Micellar Aggregates and Mesophases; A SANS Study” *J. Phys.; Condensed Matter* 8, A13 (1996).

http://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf. Check out chapters 42 and 44.